

The University of Chicago

**THE TECHNICAL EXTRACTION OF
ELEMENT 91-PROTOACTINIUM**

A PART OF A DISSERTATION SUBMITTED TO THE FACULTY
OF THE DIVISION OF THE PHYSICAL SCIENCES IN
CANDIDACY FOR THE DEGREE OF DOCTOR OF
PHILOSOPHY

DEPARTMENT OF CHEMISTRY
MARCH, 1935

By
MEYER AGRUSS

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Technical Extraction of Protoactinium

A PROCESS for the large-scale extraction of protoactinium, the longest lived isotope of element 91, is here described. This is a continuation of the technical extraction process developed¹ at the I. G. Farbenindustrie's factory in Ludwigshafen, Germany, in 1928.

Through the courtesy of Lindsay Light and Chemical Company, operating space was rented at their factory in West Chicago, Ill., where a pilot plant was installed for the conversion of the radium residues.

SOURCE OF PROTOACTINIUM

Protoactinium occurs in nature in smaller concentrations than radium. Every natural uranium mineral contains 8 grams of protoactinium for every 10 grams of radium (4). Fortunately, during the process for radium extraction from pitchblende by Mme. Curie's method, the protoactinium concentrates in the residues and gives a better starting material than is found in nature. The starting material in the present experiments was the final residue, the so-called *Rückrückstande*, from the Czechoslovakian State Mining Factory in Joachimsta, Bohemia.

The pitchblende *Rückrückstande* are in the form of a fine powder, reddish in color, and very gritty, containing smaller or larger quantities of foreign material (like bricks, stones, etc.). Its average percentage composition is as follows:

SiO ₂	60	Al ₂ O ₃	5	CaO	0.6
Fe ₂ O ₃	22	MnO	1	MgO	0.5
PbO	8				

It contained also small amounts of titanium (0.3 per cent), zirconium (0.1 per cent), and hafnium together with many other elements. Graphite occurred as an occasional impurity to the extent of 0.1 per cent. The protoactinium content was, on the average, 300 mg. of Pa₂O₅ per metric ton (a concentration of 1:3,000,000), whereas the richest pitchblendes contain about 200 mg. per ton (5).

Protoactinium has exactly the chemical properties we

¹ A complete description of this process was left in the hands of O. Hahn and later briefly described by O. Erbacher in Ullman's *Enzyklopädie der technischen Chemie*, 2nd ed., Vol. 8, p. 641 (1931). See also Grosse (2).

would expect from a higher homolog of tantalum; besides the natural analogy with the latter, it exhibits a number of individual properties (2, 3). A characteristic reaction is its complete precipitation with zirconium phosphate.

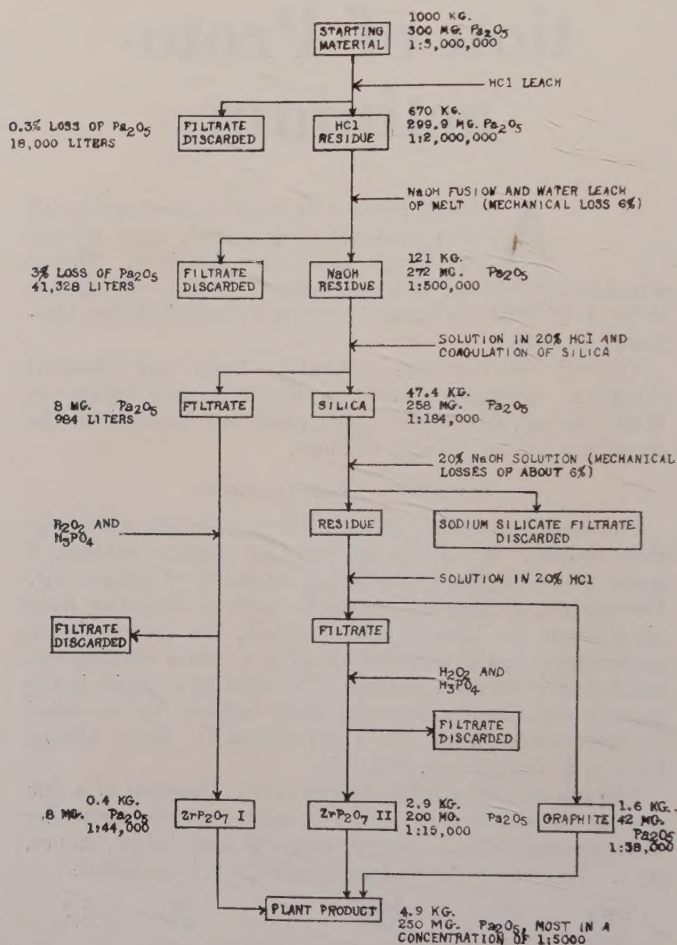


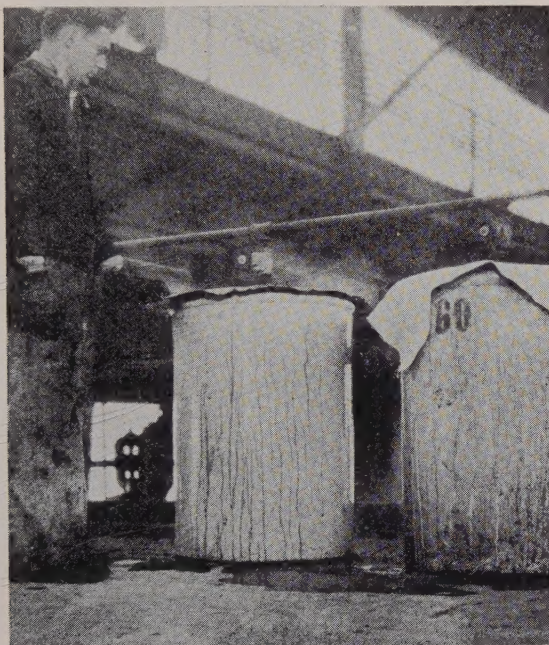
FIGURE 1. PROGRESS FOR LARGE-SCALE EXTRACTION OF PROTOACTINIUM

PLANT PROCESS

The process finally adopted for the large-scale extraction of protoactinium is shown in Figure 1. The three main steps are:

1. Hydrochloric acid leach of the starting material.
2. Sodium hydroxide fusion of the residue from the leach.
3. Water leach of the fusion and elimination of silica.

The treatment with hot 25 per cent hydrochloric acid dissolves all of the iron, the more basic oxides, and most of the lead, leaving a protoactinium concentrate consisting chiefly of silica with small quantities of zirconium, titanium, and other less basic oxides. The residue from the hydrochloric acid leach was fused with flake caustic soda to convert the silica to sodium silicate, the melt was leached with water, and the sodium silicate extract was filtered. This treatment eliminated most of the silica and all of the lead. The residue, containing most of the protoactinium, was dissolved in acid, thereby causing the precipitation of the remaining silica (from insoluble silicates). This precipitate was coagulated with steam and removed by filtration. The protoactinium



HYDROCHLORIC ACID EXTRACTION

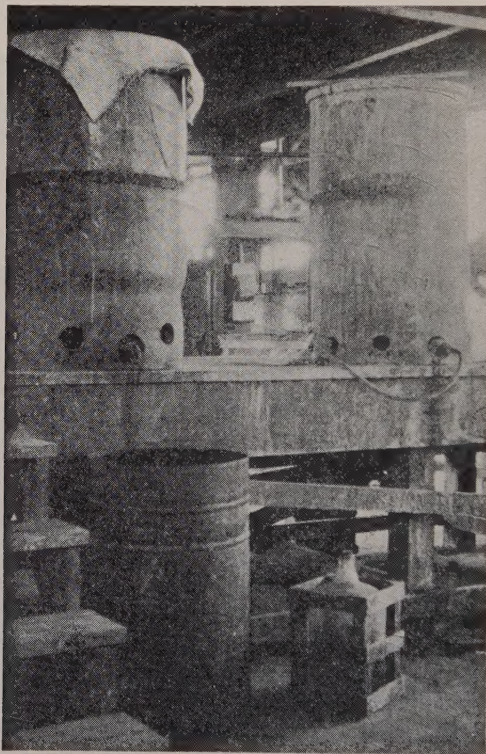
in the acid filtrate was recovered by precipitating it in the cold, together with zirconium phosphate (termed ZrP_2O_7 I), by addition of soluble zirconium salts and H_3PO_4 . The precipitated silica, containing 70 per cent of the initial protoactinium, was treated with a hot, 20 per cent sodium hydroxide solution, the extract was filtered, and the residue, consisting of oxides easily soluble in acid, was dissolved in hydrochloric acid. This acid solution was freed from graphite by filtration, and the protoactinium in the clear filtrate was precipitated together with zirconium phosphate (termed ZrP_2O_7 II). The plant product consisted of ZrP_2O_7 I, ZrP_2O_7 II, and the graphite. It weighed, on the average, 4 to 5 kg.

per metric ton of starting material and contained 80 to 90 per cent of the protoactinium, most of which was in a concentration of 1:5000.

The further concentration of this crude works material was carried out by means of laboratory methods, which led eventually to the isolation of pure Pa_2O_5 (6).

HYDROCHLORIC ACID LEACH

The acid leach of the starting material was made in 60-gallon (227-liter) stoneware crocks fitted with covers of sheet

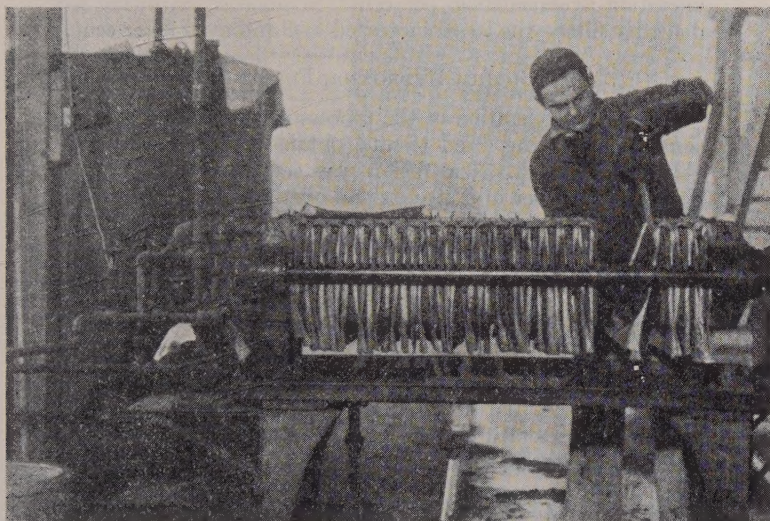


FILTERS FOR HYDROCHLORIC ACID RESIDUES

lead 0.25 inch (0.635 cm.) thick. A 1.5-inch (3.8-cm.) hole in the center of the lid served for the steam inlet and a 1-inch (2.5-cm.) hole near one side allowed for the escape of vapors. After trying many materials, including lead pipe, for a heating element, hard-glass combustion tubing was finally adopted. Live steam was used both for heating the mixture and for stirring it. In the process used previously at the I. G. Farbenindustrie factory, enameled autoclaves fitted with motor-driven anchor-shaped stirrers were used for the acid leach. These were found to be unsatisfactory because the

gritty starting material would chip the lining of the vessels and severe corrosion would take place. Stoneware crocks, which are cheaper and noncorroding, have been found to answer the purpose very well. Of course, care must be taken in the handling of these crocks. A battery of six crocks could be manipulated at the same time, each crock containing 30 kg. of starting material, 100 kg. of fuming (40 per cent) hydrochloric acid, and 44 liters of softened water.

The material in each crock was heated for 2 hours at 95°C . To avoid cracking the crock while bringing it up to temperature, the heavy starting material was allowed to settle to the bottom and the steam valve was opened very slightly. The bumping, caused by the live steam coming into the warm (35°C .) mixture, was absorbed by the layer of material at the bottom of the crock. After 15 minutes of slow heating,



FILTER PRESS FOR SILICA RESIDUE; PRECIPITATION TANK AT LEFT

the contents reached a temperature of 90° to 95°C ., after which the steam was admitted at such a rate as to stir the material in the crock.

The heated material was allowed to settle and the hot solution was separated from the residue by a stoneware suction filter, 400 liters in capacity, with duck cloth as a filter medium. The residue was then washed free from acid and iron with 400 liters of hot, soft water. This treatment dissolved all of the iron and most of the lead, leaving a residue consisting chiefly of silica and containing zirconium, titanium, hafnium, tantalum, and other less basic oxides. It was found that about 5 to 10 per cent of the protoactinium in the starting material also dissolved in the hydrochloric acid; therefore it was precipitated from solution by adding, intermittently,

small amounts of a zirconium oxychloride solution and a fivefold excess of phosphoric acid during the leaching period until a total of 20 grams of zirconium dioxide was added to each leach of 30 kg. (corresponding to 650 grams of zirconium dioxide per ton of residues). The precipitated zirconium phosphate took with it any protoactinium in solution. In this way the loss of protoactinium in the acid leach was brought down to less than 0.5 per cent. The added zirconium also served as the carrier for protoactinium through the entire process; if the original zirconium content of the starting material is appreciably higher a smaller quantity than given above can be added.

By the foregoing method the hydrochloric acid leach removed an average of 33 per cent soluble material; in other words, from each charge of 30.0 kg. a residue of about 20.0 kg. was obtained. The protoactinium loss during the whole operation averaged 0.35 per cent; in some cases, owing to defective filters, the losses increased to 1 and even 2 per cent.

SODIUM HYDROXIDE FUSION

The second operation of the process consisted of a caustic soda fusion of the dried residue obtained from the hydrochloric acid leach. The fusion was carried out in a steel cylindrical pot set in a steel tripod over a gas burner. Fire brick and sheet asbestos surrounded the pot to eliminate heat losses.

The residue from the acid leach (10 kg.) and flake caustic soda (30 kg.) were thoroughly mixed. Half of this mixture was placed in the pot and heated until the reaction ceased; the remainder of the mixture was added gradually to the molten material. When all the mixture had melted and the reaction ceased, the liquid was stirred and heated until it reached a temperature of about 700° to 800° C. in order to reduce completely the small amount of lead still present to the metallic state. The metal was free from protoactinium; its reduction was probably due to the carbon present in the original ore.

Each fusion required 2 hours for melting and heating to the final temperature, and consumed a total of about 600 cubic feet (16.8 cubic meters) of gas. The very light and fluffy residue from the first operation caused some loss (about 6 per cent) during the process of fusion, even though the melting pot was covered. This loss has, however, been greatly decreased by deflecting the upward rush of air from the burner. It can also be eliminated by moistening the melting mixture with a very concentrated (70 per cent) solution of sodium hydroxide before placing it in the melting pot.

LEACHING OF MELTS

The third step in the process was a water leach of the cooled caustic soda melt. Eight such melts were combined and leached with 2600 liters of hot, soft water in a 3200-liter

steel tank. The residue was washed by decantation five or six times before it was separated from the supernatant liquid by a plate and frame filter press. The material in the filter press was washed with hot, soft water until free from alkali and was dried with compressed air.

The average dry weight of the residue from the caustic soda leach was 3.6 kg. from 30 kg. of starting material, and the yield of protoactinium at this point was between 85 and 90 per cent. Table I shows the protoactinium content of the residue obtained from the water leach of the melts and Table II shows the loss of protoactinium during this operation. The data in Table II may give the impression that large losses of protoactinium occurred during the melting and leaching operations. It must be borne in mind that, when the caustic soda leach is washed by decantation, a perfectly clear supernatant liquid cannot be obtained unless a day is allowed for each settling. Therefore, the small loss due to a few fine particles in the supernatant liquid was completely counterbalanced by the saving of time and labor involved.

TABLE I. PROTOACTINIUM CONTENT OF RESIDUE FROM WATER LEACH OF MELTS

Run No.	Residue from Leach, Kg.	Per Cent of Initial Ore	P ₂ O ₅ Content, Mg. ^a	Yield, Per Cent
6 plus 7	7.7	12.8	16.3	90.5
8 plus 9	7.3	12.1	15.4	85.5
10 plus 11	7.3	12.1	15.9	88.3
12 plus 13	6.1	10.2	16.0	88.8

^a Average P₂O₅ content of initial material is 18 mg.

TABLE II. LOSS OF PROTOACTINIUM DURING LEACHING OF MELTS

Run No.	Water for Leach, Liters	P ₂ O ₅ Loss, Per Cent of Initial
1	1280	5.0
2	1280	1.2
12 plus 13	2560	3.0
14	1280	5.1

PRECIPITATION OF REMAINING SILICA

The residue from the caustic soda leach was dissolved in 20 per cent hydrochloric acid in a 60-gallon (227-liter) crock, and the remaining silica was coagulated by passing steam into the acid solution until it reached 95° C. The coagulated silica takes with it 80 per cent or more of the protoactinium in the residue from the caustic soda melt, as well as 90 per cent of the zirconium hydroxide in the same residue. Table III shows the protoactinium content of the coagulated silica.

To the cold acid filtrate, obtained from the silica, was added an excess (250 to 300 cc.) of 30 per cent hydrogen peroxide (to oxidize the titanium to pertitanic acid and prevent its coprecipitation) and an excess (250 to 300 cc.) of 20 per cent phosphoric acid. The precipitated zirconium phosphate took with it the protoactinium (usually 2 mg. or less from 240 kg. of starting material) still contained in the acid filtrate and was termed ZrP₂O₇ I.

Originally it was intended that this operation should consist of dissolving the whole residue from the caustic soda leach in acid and precipitating all the zirconium as a phosphate from this acid solution. Quite unexpectedly this proved to be a troublesome operation under the conditions of these experiments. When the residue from the leach was dissolved in 20 per cent acid (sulfuric or hydrochloric), a thick gelatinous mixture was obtained because the starting material contained undecomposable, water-insoluble silicates which were decomposed by the acid and gave free silicic acid. Remelting of the residue did not completely eliminate the silica arising from these undecomposable silicates. However, it was noticed that if live steam was passed into the gelatinous acid solution until it reached 95° C., the silica separated out in globules which settled quickly and filtered easily. This precipitation was later used to advantage in that it provided a concentrate from which the protoactinium could be easily separated and allowed to minimize the amount of zirconium oxide added during the first operation of the process.

TABLE III. PROTOACTINIUM CONTENT OF SILICIC ACID PRECIPITATED IN PLANT PROCESS

Run No.	Silicic Acid, Grams	P ₂ O ₅ , Mg.	Yield, Per Cent
2	1,250	7.8	86.3
12 plus 13	3,264	16.5	91.7
15	570	7.6	85.0
16	4,835	8.0	90.0
20-23, inclusive	20,339	38.7	83.2

TREATMENT OF PRECIPITATED SILICA

The silica, collected from sixteen caustic soda melts (corresponding to 240 kg. of original starting material), was treated in an iron tank with a hot, 20 per cent sodium hydroxide solution. This treatment dissolved most of the silica and the small amount that remained could be easily handled in subsequent operations. The residue from this treatment was washed by decantation and separated from the supernatant liquid by means of a plate and frame filter press. The moist residue, consisting of a small amount of silica and basic oxides easily soluble in acid, was dissolved in 20 per cent hydrochloric acid, the solution filtered free from graphite, and the clear filtrate treated at room temperature with an excess of 30 per cent hydrogen peroxide and 20 per cent phosphoric acid as previously described for ZrP₂O₇ I. The zirconium phosphate thus obtained contained the protoactinium which remained with the silica and was termed ZrP₂O₇ II.

PLANT PRODUCT

The ZrP₂O₇ I and II, together with the graphite, comprised the plant product. Each of these three products still contained substantial quantities (about one-third) of silica and was worked separately. The ZrP₂O₇ II contained, on the average, 70 per cent of the protoactinium in the starting ma-

terial, the ZrP_2O_7 I contained an average of 3 per cent, and the graphite an average of 15 per cent, giving an average yield of 85 to 90 per cent for the plant product. The plant product, after eliminating the phosphoric acid and silica (KOH-melt), contained most of the protoactinium in a concentration of 1:5000, whereas the starting material contained the protoactinium in a concentration of 1:3,000,000. Table IV shows the yield of protoactinium in the plant product.

TABLE IV. YIELD OF PROTOACTINIUM IN PLANT PRODUCT

Run No.	Ore, Kg.	— ZrP_2O_7 I— Pa_2O_5 , Grams Mg.		— ZrP_2O_7 II— Pa_2O_5 , Grams Mg.		—Graphite— Pa_2O_5 , Grams Mg.		Total Pa_2O_5 , Mg.	Yield, Per Cent
		Grams	Mg.	Grams	Mg.	Grams	Mg.		
20-27	230	95.6	1.8	765.4	48.2	250.0	5.0	55.0	82.6
28-35	225	75.5	1.0	761.5	32.8	208.7	20.0	53.8	83.9
36-43	222	84.3	1.2	901.7	49.7	400.0	4.0	54.9	82.3
44-51	225	90.0	2.0	500.0	49.3	130.0	4.5	55.8	82.0

Since the plant product contained the protoactinium in so high a concentration, it was advisable to carry out the further purification in the laboratory. To date 1200 kg. of original residues have been processed and 250 mg. Pa_2O_5 have been obtained in a concentration of 1:5000 or higher. One hundred milligrams of this protoactinium have been isolated in the pure state as the pentoxide (6), Pa_2O_5 . Larger quantities will be extracted in the future.

In order to follow the protoactinium during the process, it is imperative to run control analyses, if possible, after each operation. Owing to the fact that protoactinium is a radioactive element emitting alpha particles, it can be easily traced through the subsequent steps of its concentration by means of an ordinary Rutherford alpha-electroscope. Since other radioactive elements are also present in the residues, the protoactinium has to be chemically separated from them before its alpha activity is measured. (For analytical procedure see citation 4.)

DISCUSSION

The present process differs from the process used by Grosse² in that it uses silica besides zirconium phosphate as a carrier for protoactinium. Since the silica can be easily separated from the protoactinium by means of sodium hydroxide, it simplifies matters greatly.

The same process, with appropriate adjustments, could be used for residues from any pitchblendes. For carnotites or other material the same principle—i. e., bringing the protoactinium in acid solution and precipitating with zirconium phosphate and silica—should also prove successful.

Recently this process for extraction of protoactinium has been successfully used in Germany by Graue and Käding (1) who were able to extract from 5 tons of the same residues 0.7 gram Pa_2O_5 . The only changes these authors made were the reversing of sequence—i. e., first melting the original material in caustic soda and then making a hydrochloric acid leach with the residue obtained from the melt. This is a

disadvantage because larger amounts of silica are left in the residue from the melt and cause difficulties in the hydrochloric acid extraction. These difficulties induced Graue and Kädin to eliminate large quantities of silica by fuming with hydrofluoric and sulfuric acids, a troublesome operation on a technical scale. Furthermore these workers used exceedingly large amounts of zirconium oxide (25 kg.) which causes great difficulties in filtration and handling and which are absolutely unnecessary. One-tenth of this quantity would be sufficient, as can be seen from the present results.

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